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(58) Field of Search

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ONLINE DATABASES: WPI AND CALIMS

(54) Catalyst pack

(57) A catalyst pack (10) in which a quantity of a relatively expensive material such as platinum is replaced by a greater quantity of a relatively inexpensive material such as palladium in the upstream region of the pack. As shown, palladium gauges 16 are interleaved with gauges 12, 12' in the upstream region.

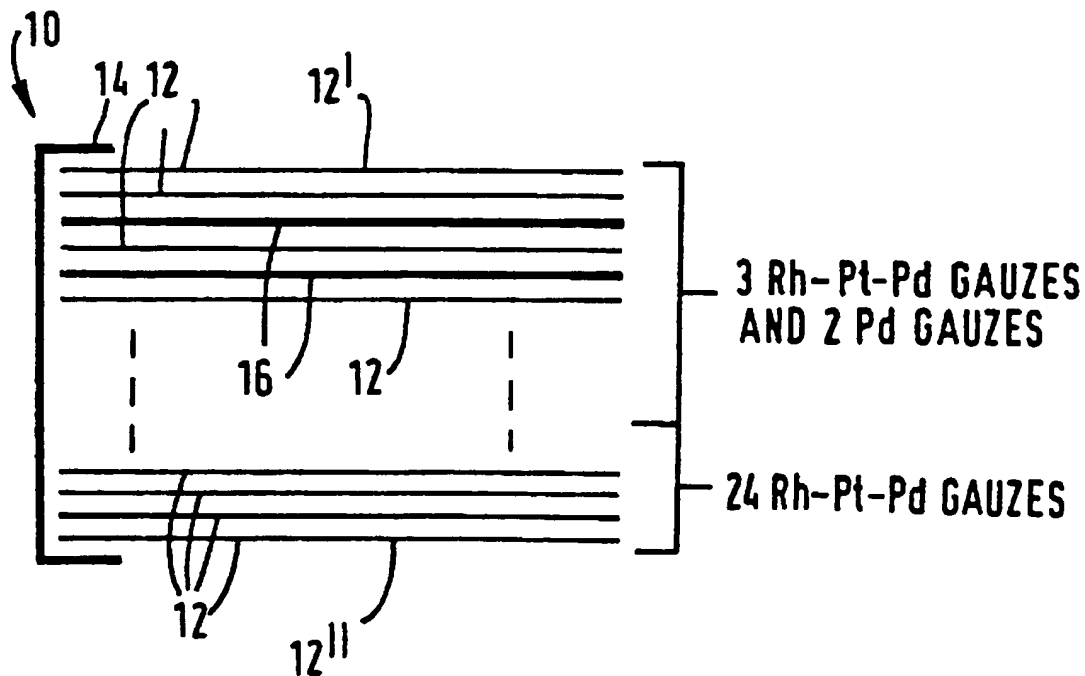


FIG. 1

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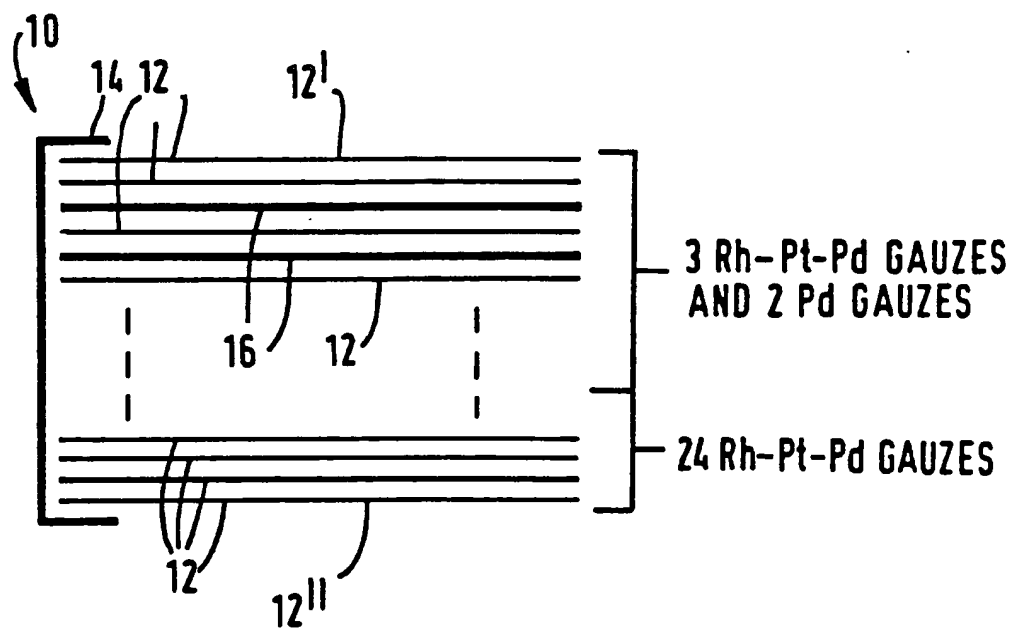


FIG. 1

CATALYST PACKS

This invention relates to catalyst packs, which normally comprise a plurality of foraminous sheets arranged in layered relation.

- 5 In use, catalysts can suffer greatly from material losses through volatilisation, especially during highly exothermic reactions such as the oxidation of ammonia. Where the catalyst is of precious metal (for example, platinum alloys are usually used in the oxidation of ammonia), this loss can be extremely
10 expensive and has a major bearing upon production costs. The initial capital cost of the pack is also a major consideration. Consequently, there is an ongoing development effort concentrating upon the efficient use of precious metals in catalyst packs.
- 15 One result of this development effort is disclosed in UK Patent Application No. 2062486. This document refers to a catalyst pack of woven metallic gauzes in which at least some of the gauzes disposed at or towards the front or upstream end of the pack are made from wire having a greater cross-
20 sectional area than the wire making up at least some of the gauzes disposed at or towards the rear or downstream end of the pack. This 'tailoring' of the wire sizes is intended to reflect the well-known metal loss characteristic in which more metal tends to be lost from the relatively upstream gauzes
25 than is lost from the relatively downstream gauzes. Thus, the durability of each gauze is selected to suit the rate at which it is expected to erode. In this way, no more of the expensive catalytic material is used than is necessary; in effect, the amount of catalytic material in the lightly-loaded downstream
30 region of the pack is reduced to a minimum. Thus, the capital cost of the pack is also minimised for a given capital outlay.

International Patent Application No. WO92/02300 discloses a so-called 'self-gettering' catalyst pack in which the platinum

saved in the downstream region by 'tailoring' is replaced to some extent by palladium which acts both as a getter for the remaining platinum layers and as a catalyst in the oxidation of ammonia. In that reaction, palladium is less efficient as
5 a catalyst than platinum but is so much cheaper that, for a given unit cost, sufficient extra palladium may be used to more than compensate for its lack of catalytic efficiency.

Thus, the self-gettering catalyst pack of International Patent Application No. WO92/02300 has a relatively high platinum
10 content in its upstream region and relatively high palladium content in its downstream region. As such, it reflects conventional wisdom among those skilled in the art of catalysis, which is to place the better catalytic material (platinum) at the position in the pack of the heaviest
15 expected duty and to use the lesser catalytic material (palladium) principally as a getter and thus largely downstream of the platinum-rich upstream region.

The present invention, quite literally, turns conventional wisdom on its head. Applicant has found that, surprisingly,
20 performance improvements may be obtained by inverting the pack disclosed in International Patent Application No. WO92/02300. In particular, the invention reduces back-pressure and allows longer runs or 'campaigns' before the pack needs replacement.

Thus, this invention contemplates a catalyst pack comprising
25 first and second catalytic materials, the first catalytic material being relatively inexpensive but relatively inefficient, and the second catalytic material being relatively expensive but relatively efficient, wherein the upstream region has a relatively high content of the first
30 catalytic material.

The invention may also be expressed as a mixed pack of first and second catalytic materials as defined above, in which the first, relatively inefficient and inexpensive catalytic

material is distributed approximately to conform to an upstream-biased material loss profile.

Preferably, the first catalytic material is palladium or a palladium-based alloy and the second catalytic material is platinum or a platinum-based alloy. At the time of writing, platinum is approximately four times as expensive as palladium, per unit weight. Platinum is also 1.75 times denser than palladium. Given the cost and density differences, approximately seven units of palladium correspond to one unit of platinum for the same overall cost. So, in a catalyst pack for example, one platinum gauze may be replaced by seven similar palladium gauzes without adding to the material cost of the pack. In many cases, such a quantity of palladium is sufficient to outweigh the intrinsic disadvantages of palladium in terms of catalytic effect, so that the catalytic efficiency of the pack is actually increased.

The invention allows an increase in the average life of a catalyst pack, without necessarily adding to material costs, detracting from catalytic efficiency, or worsening metal loss characteristics. Increasing the life of the pack reduces plant shutdowns and thus minimises expensive downtime. How the invention achieves this is not yet fully clear, but it is likely that the run length is increased simply because the palladium elements, being thicker and/or more numerous than platinum elements for a given cost, can erode for longer before they finally wear away or become uneconomic to use. In addition, some studies suggest that the addition of palladium increases the resistance of a catalyst unit to degradation by organic contaminants, notably (but not exclusively) oils which may be introduced from the ammonia feed, compressor bearings etc.

Effectively, then, the present invention preserves the better and more expensive catalytic material - e.g. platinum - by using a less expensive substitute in the region of the pack

that is known to suffer most from loss of metal through volatilisation.

Also, palladium is a getter for volatilised platinum and, even though situated in the upstream region of the pack, a
5 palladium layer can be downstream of or adjacent to a platinum layer. In that position, the palladium layer will recover some platinum eroded from the platinum layer by the stream of reactants.

Elements of the respective catalytic materials may be
10 separated from one another by support elements. The support elements can, for example, be stainless steel gauzes. Other types of support element include ceramic elements or Pt/Pd/Rh-coated inert elements.

The second catalytic material is suitably Pd with additions
15 of iridium, ruthenium, molybdenum, cobalt, manganese or zirconium. The first catalytic material is suitably a Rh-Pt-Pd alloy, with Rh present in an amount between 1 and 15 wt%, and with Pd present in an amount between 1 and 30 wt%, preferably with additions of iridium, ruthenium, molybdenum, cobalt,
20 manganese or zirconium. A US alloy, 5%Rh-90%Pt-5%Pd, is a specific example.

At present, rhodium is approximately forty times as expensive as palladium, weight for weight. Thus, a reduction in the amount of rhodium (e.g. by deleting a Rh-Pd-Pt gauze) involves
25 a substantially greater cost saving than simply removing some platinum. This saving can be used to pay for still more palladium, to the further benefit of the unit's performance.

Elements of the first and second catalytic materials may alternate with each other in the unit.

30 The elements of the first and second catalytic materials are preferably of wire, which elements are woven, knitted or

otherwise connected to form a gauze screen or sheet. Knitting is preferred for optimum flexibility, durability and ease of manufacture. The sheet may be substantially flat or may have a relief pattern applied thereto.

- 5 Mesh sizes for the gauze of the first catalytic material can range from, say, 30 to 1200 meshes per cm^2 , and preferably from 50 to 1000 meshes per cm^2 . Wires of the first catalytic material are suitably in the range 0.05 mm to 0.25 mm.

- Mesh sizes for the gauze of the second catalytic material can
10 range from, say, 100 to 1500 meshes per cm^2 , and preferably from 200 to 1200 meshes per cm^2 . The wires of the second catalytic material can range, for example, from approximately 0.05 mm to 0.3 mm, and preferably from 0.05 mm to 0.15 mm in diameter.

- 15 Where the second catalytic material is platinum or a platinum alloy, it is preferred that the first catalytic material is substantially free of gold. Gold is known to be a poison for platinum catalysts in the oxidation of ammonia. This can cause considerable difficulties, particularly bearing in mind that
20 the gauzes of the first catalytic material are in close proximity with, and generally upstream of, the platinum gauzes. Thus, the use of substantially gold-free materials avoids poisoning of the platinum by any gold that could otherwise enter the stream of reactants through volatilisation
25 from the layers of the first catalytic material.

- Unfortunately, gold is generally used in palladium alloys for its strengthening effect, and its removal can unacceptably weaken a palladium alloy gauze under the arduous reaction conditions common in catalysis. For this reason, in some
30 embodiments of the invention, gauzes of substantially gold-free palladium or palladium alloy are supported by support means.

Support means may be done away with or reduced if the palladium is strengthened. Thus, a further embodiment of the invention contemplates gauzes of substantially gold-free palladium alloyed with at least one element selected from the
5 group rhenium, iron, molybdenum, zirconium, tantalum, tungsten, cobalt, yttrium, thorium, ruthenium, iridium, osmium, rhodium, nickel, copper and chromium.

In Pd-Zr alloys, it is preferred that zirconium content does not exceed 2 wt%. In alloys of palladium with any other
10 element in the group, it is preferred that the content of that other element does not exceed 8 wt%.

In general, it is desirable for an alloying element to increase the melting point of palladium (or at least not to reduce its melting point unduly), thereby minimising self
15 diffusion and grain growth, and resultant expansion effects, under high-temperature conditions in use, which can occur with pure palladium. Also, as gettering depends upon diffusion of platinum into the lattice of the catchment material, gettering efficiency may be expected to increase as the lattice constant
20 of palladium is increased. It is therefore also desirable that the alloying element acts to increase the lattice constant of palladium.

Of the elements in the specified group:

(i) rhenium causes little or no reduction in melting point
25 and, in small quantities, increases hardness markedly. Also, platinum readily alloys with rhenium.

(ii) iron increases the lattice constant, and is very cheap;

(iii) molybdenum increases the melting point of the alloy.

(iv) addition of zirconium does not significantly reduce the
30 melting point of palladium and increases its lattice constant.

also, zirconium can be slagged off as the oxide on melting. It is also envisaged that a degree of internal hardening may take place in use. Zirconium may even be partially or fully oxidised before use to produce a dispersion strengthened alloy
5 with excellent high temperature characteristics.

(v) tantalum increases the melting point of the alloy.

(vi) tungsten raises the melting point of palladium considerably whilst largely maintaining its lattice constant.

(vii) cobalt can become oxidised in use to form cobalt oxide,
10 which is itself a catalyst in the oxidation of ammonia. Thus, it is envisaged that cobalt may enhance the catalytic properties of palladium when used for this reaction.

(viii) ruthenium, iridium, osmium and rhodium all raise the melting point of palladium.

15 The invention encompasses the use of a catalyst pack as herein defined, and any substances produced by the use of such a pack.

In order that this invention may be more readily understood, embodiments thereof will now be described, by way of example
20 only, with reference to the accompanying drawing, Figure 1. Figure 1 is a schematic partial cross-sectional view through a catalyst pack constructed in accordance with this invention.

Referring to Figure 1, a catalyst pack 10 comprises a plurality of catalytic gauzes 12 disposed between a top gauze
25 12' and a bottom gauze 12". The top gauze 12' and the bottom gauze 12" are connected by a heat-resistant nickel alloy foil 14 which overlaps an edge portion of the top and bottom gauzes 12' and 12". Thus, in outward appearance, the pack 10 is similar to known catalyst packs.

Within the pack 10 and disposed between the top and bottom gauzes 12', 12" is a total of twenty-five gauzes 12. The gauzes 12, 12' and 12" are identical to one another, in the example being of 5% Rh - 90% Pt - 5% Pd wire although the composition may be varied without departing from the inventive concept. Additionally, the pack 10 contains two gauzes 16 of palladium wire.

Moving downstream through the pack 10 from top to bottom as illustrated, there are two Rh-Pt-Pd gauzes 12', 12, one Pd gauze 16, one Rh-Pt-Pd gauze 12, one Pd gauze 16, and twenty-four Rh-Pt-Pd gauzes 12, 12".

As can be seen, the Pd gauzes 16 are in the upstream region of the pack 10 and thus are positioned in the region of maximum metal loss expected from the typical upstream-biased metal loss profile.

Further, the Pd gauzes are supported by the Rh-Pt-Pd gauzes, although other support means such as stainless steel support meshes may be used if desired.

Many variations are possible without departing from the inventive concept of the present invention. For example, the numbers of the respective gauzes or their wire thicknesses may be varied considerably, if it is desired more finely to 'tailor' the amount of Pd to the expected metal loss profile.

Further, it is not essential that the downstream portion of the catalyst pack is free of palladium gauzes. Indeed, there may be benefit in an increased quantity of palladium gauzes near the downstream end of the pack, to act as a getter for the platinum gauzes upstream thereof.

More generally, it is believed that the invention will give benefit with many combinations of catalytic materials, provided that there is a cost disparity between them

sufficient to offset any catalytic shortcomings of the cheaper material. All such combinations are considered to fall within the broadest concept of the invention.

CLAIMS

1. A catalyst pack comprising a mixture of foraminous layers of different catalytic materials having disparate costs, in which the relatively inexpensive catalytic material is distributed approximately to conform to an upstream-biased metal loss profile.
2. A catalyst pack according to claim 1, wherein the catalytic materials are platinum and palladium, or alloys thereof.
3. A catalyst pack according to claim 2, wherein the palladium or palladium alloy is substantially free of gold.
4. A catalyst pack according to claim 3, wherein the palladium is alloyed with at least one element selected from the group rhenium, iron, molybdenum, zirconium, tantalum, tungsten, cobalt, yttrium, thorium, ruthenium, iridium, osmium, rhodium, nickel, copper and chromium.
5. A catalyst pack according to claim 3 or claim 4, wherein the palladium or palladium alloy is supported by support means.
6. A catalyst pack according to any preceding claim, wherein the relatively inexpensive material is distributed by the inclusion of more or less layers thereof in a given region of the pack.
7. A catalyst pack according to any of claims 1 to 5, wherein the relatively inexpensive material is distributed by varying the thickness or spacing of elements making up a foraminous layer thereof.
8. A catalyst pack according to any preceding claim, wherein the relatively inexpensive material is present in an increased

quantity in the downstream region of the pack in order to act as a getter for the relatively expensive material.

9. A catalyst pack, substantially as hereinbefore described or with reference to the accompanying drawing.

5 10. The use of a catalyst pack as defined in any preceding claim.

11. Any substance produced by use of a catalyst pack as defined in any of claims 1 to 9.

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

Applica number

GB 9300157.6

Relevant Technical fields

(i) UK CI (Edition L) B1E; B1F

(ii) Int CI (Edition 5) B01J; C01B

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES : WPI AND CLAIMS

Search Examiner

J H WARREN

Date of Search

15 FEBRUARY 1993

Documents considered relevant following a search in respect of claims 1-10

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 0988244 A (UNIVERSAL OIL) whole, especially page 2 lines 6-11 and page 6, lines 28-33	1, 2

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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